

SEDIMENT ANALYSIS

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THE ONTARIO WATER RESOURCES COMMISSION

SEDIMENT ANALYSES

INTRODUCTION

Deterioration of water quality in lakes and rivers by industrial and domestic effluents and the process of eutrophication is normally accompanied by some corresponding changes in the chemical and biological composition of the sediments (Veal and Osmond 1968, Bennett and Brydges 1969). Many of the wastes discharged to waterways, in both particulate and dissolved forms, become resident in the sediment. The sediments have not been as intensely monitored as the water itself, partly because they have less direct effect on most water users. There has recently been an increasing interest in the composition and properties of the sediments for two main reasons; (1) the need for information of their effects on pollution control measures relating to nutrient removal now being considered; (2) the possible need for controls on dredging operations which result in considerable mixing and redistribution of water and sediments. Dredging is usually done in harbours where the sediments have been most seriously affected by waste inputs.

While it is desirable to know the exact chemical composition of sediment, it is not easy to relate such data to either present or future water quality. It is more important for the two cases above to define how much of any given material can be released from the sediment if the input is curtailed and how much can be released under mixing conditions analogous to dredging procedures.

Realistic field measurements of the exchange of ions between sediments and water are very difficult to make, (Gahler 1969). Any apparatus placed in the system to contain the exchanging ions can itself alter the ratios and types of exchange by disturbing normal currents. In addition, there are the logistical problems of conducting experiments in deep water.

Since the amount of any given constituent which is either readily soluble or potentially soluble is more important than the total quantity in the sediment, numerous extraction procedures have been developed which try to define the soluble fractions. Mortimer, 1941, used a small tank as a closed system in order to evaluate the effect of sediments on the overlying water. He identified the important principle of phosphorus release from iron compounds in the sediments under anaerobic (reducing) conditions. Significant fractions of the phosphorus in the mud is bound to ferric oxides and/or hydroxides. Under reducing conditions the ferric iron is reduced to the ferrous form which is soluble. The iron, as well as the adsorbed phosphorus, is then released to the overlying water. McPherson, et. al. 1958, conducted a series of phosphorus extraction experiments using a variety of sediments and extracting with solutions of pH over the range of 3 to 9. They used both dry and ashed sediment and while striking effects of pH were observed, particularly with ashed material, the results were not related to observed field measurements.

More recently, Wentz & Lee, 1969, devised and applied an extraction procedure using HCl - H₂SO₄ mixtures. They based the concept on work reported by Jackson, 1965, in which a correlation was observed between crop response and the acid extractable phosphorus. The relationship only held for acid soil. The soils used in Wentz and Lee's study contained large fractions of calcium carbonate. The results were related to some historical changes in Lake Mendota but were not used to make predictions regarding recycling of phosphorus.

While many attempts have been made to determine the extent of nutrient recycling via the study of controlling mechanisms (Olsen 1964, Gumerman 1970) their overall success seems rather limited.

In 1969 the OWRC began three independent research projects requiring an evaluation of the condition of the sediments and their possible effects on lake water. Each of these projects included extensive chemical and biological analyses of the lake waters, and therefore afforded an excellent opportunity to study recycling of nutrients and other elements. One of these projects is designed to determine extent, causes and possible cures for eutrophication in the Lakes Muskoka, Rosseau and Joseph chain. Eight stations were selected in areas ranging in condition from nearly pristine up to a substantial degree of eutrophication. Sediment samples were collected once a week from the two stations at the extreme ends of the productivity scale and once a month from the other six stations.

Another of the projects involved the sampling of small lakes in the Elliot Lake area in preparation for controlled addition of nutrients. Sediment samples were collected once in September. They are referred to in the text as the "Northern Lakes".

The third project is a cooperative study between the OWRC Biology Branch and the Ontario Department of Lands and Forests Research Branch and is aimed at determining the factors responsible for growths of various aquatic plants in small lakes and ponds. In this project 37 stations in 17 lakes and ponds representing a wide range of chemical, biological and physical conditions were sampled one to four times during the summer. Since these waters are privately owned they are identified by code numbers. They are referred to collectively in the text as the "plant ecology study".

METHODS

The bulk of evidence reported in the literature suggests that only the top 1 to 10 mm of sediments are in active exchange with the overlying water. (Zicker et al 1969). For this reason a standard collection procedure was adopted whereby the top centimeter was removed from samples collected in an Eckman dredge. Enough material was collected to fill a 4 oz. jar and refrigerated until use, which was normally several days after collection.

The approach selected for this study involved both the determination of total quantities of various elements in the sediment and an estimate of the amount of these elements which can be extracted with water.

Sediment Preparation

A portion of the sample was dried at 110°C and ground to a fine powder in a porcelain mortar. It can be very difficult to obtain a small representative aliquot, particularly if there are any pebbles or other coarse material present. The Cleveland office of the F.W.P.C.A. 1969, has developed a sediment analysis method including a screening procedure. By removing the largest particles it is easier to obtain aliquots and although the technique may not be wholly satisfactory, it is probably the only practical solution. By good fortune, nearly all of the samples involved in this work were of such consistency that they could be ground very fine and reproducible aliquots were easy to obtain. In a few cases, stones of one inch diameter or more were present but they were easily removed. No effort was made to remove small shells which could be ground up. The analyses have not included any mineralogy.

Nitrogen and Phosphorus

The general importance of nitrogen and phosphorus in the process of eutrophication, makes their measurement essential to any sediment study. Iron and manganese were also routinely measured as well as the loss on ignition and the weight of dry residue per unit volume of wet sediment.

Twenty milligrams of dry sediment was digested with 5 ml of 20 percent H_2SO_4 until fuming and then sufficient potassium persulphate was added to give a clear solution which was again digested to fuming until any excess persulphate was destroyed. The digest was adjusted to pH 4, diluted to 50 ml and nitrogen and phosphorus were determined by routine OWRC methods.

Iron, Manganese, Calcium, Loss on Ignition

Forty milligrams of sample was digested for 15 minutes in 10 ml of 20 percent sulphuric acid and sufficient potassium persulphate to give a clear solution. The digest was diluted to 150 ml. Iron was measured by the o-phenanthroline method and Mn and Ca were measured with an atomic absorption spectrophotometer. Two major problems were found; interference between iron and phosphorus in the phosphorus test, and an unidentified interference in some of the calcium tests. All elemental analyses were carried out in duplicate and if the results did not agree to within 10 percent then a second pair was analyzed.

The loss on ignition test was carried out according to Standard Methods, employing an ignition temperature of $600^{\circ}C$.

Extraction Test -(Triple A)

In nature, sediments are subjected to two general conditions - aerobic and anaerobic, which are characterized by extreme differences in their inherent chemical and biological processes, and are known to decidedly affect sediment water exchanges. Therefore a procedure has been developed in this work which measures the amount of nutrients released to a volume of water under these contrasting conditions.

The method used distilled water, rather than acids and bases, and is carried out on wet sediment in an attempt to keep the bacterial population intact. No attempt has been made to completely define specific mechanisms.

The objective of the test was to provide a guide to the quality of sediments analogous to the use of the BOD test as a guide to the strength of wastes. The test has been carried out in combination with analysis of the total concentrations in the original sediments.

The extraction test has been named Triple A for aerobic-anaerobic.

Preliminary experiments were conducted on Lake Erie sediments which had been dried at room temperature over several weeks time. Variable amounts of phosphorus which were released to the water under both aerobic and anaerobic conditions related to the known water quality in the areas of collection. (Bennett & Brydges, 1969). Although the technique had many experimental shortcomings, results indicated that a simple extraction test could be used as a guide to the overall quality of the sediment.

Prior to applying the test to the current projects a number of modifications and standardizations were made. A procedure was developed which used wet sediment for the extraction tests; in order to keep the sediment and bacterial population as close as possible to their original condition. A small brass scoop which had a volume of 1.19 cc was used to obtain a reproducible fixed volume sample of wet sediment. For a given sample, the dry weight of material obtained in the scoop was reproducible to better than 5 percent.

One sample of sediment was placed in each of three tared evaporating dishes which were dried at 110°C . In this way, all tests conducted on the wet sediment could be related to a dry weight of sediment.

One sample was placed in each of four 175 ml Prince of Wales bottles. Two of these were filled leaving about 2 cc of air at the top; the other two were completely filled and 50 mgm of Na_2SO_3 was added to remove any dissolved oxygen. All four were stored at 5°C for seven days with periodic mixing. The effect of temperature was not examined in detail beyond demonstrating that

variations in temperature exerted an effect and must be controlled. Five degrees centigrade was selected because incubator space at that temperature was available and it is also close to the yearly average temperature of the sediments. Preliminary experiments had shown that phosphorus concentrations increased for up to four to five days, so seven days was selected to allow ample time for equilibration.

After seven days the samples were filtered through glass fiber and routine chemical analyses applied for total and soluble phosphorus, total Kjeldahl nitrogen, nitrate, iron and manganese.

The results for the extracts in concentration units were expressed as milligrams of material released per gram of dry weight, the latter value being obtained from the average dry weight of the three samples in the evaporating dishes.

¹ RESULTS AND DISCUSSION

Four of the Lake Muskoka stations were located in bays and 4 in the open lakes. One bay was receiving treated domestic wastes and one was in an area of dense cottage development. The other stations were located in areas of less development. The sediment analytical data for each station has been averaged for use in this report.

The 3 Northern lakes sampled did not receive any known human waste inputs. They range from 2.4 to 6.9 hectares in area and from 11 to 14 meters average depth. Ten areally distributed samples were collected once from each lake and the analytical data has been averaged.

The lakes in the plant ecology study are briefly described in Table I. The analytical data has been averaged for each station.

¹The analytical data for the sediments is given in Appendix 2.

TABLE I

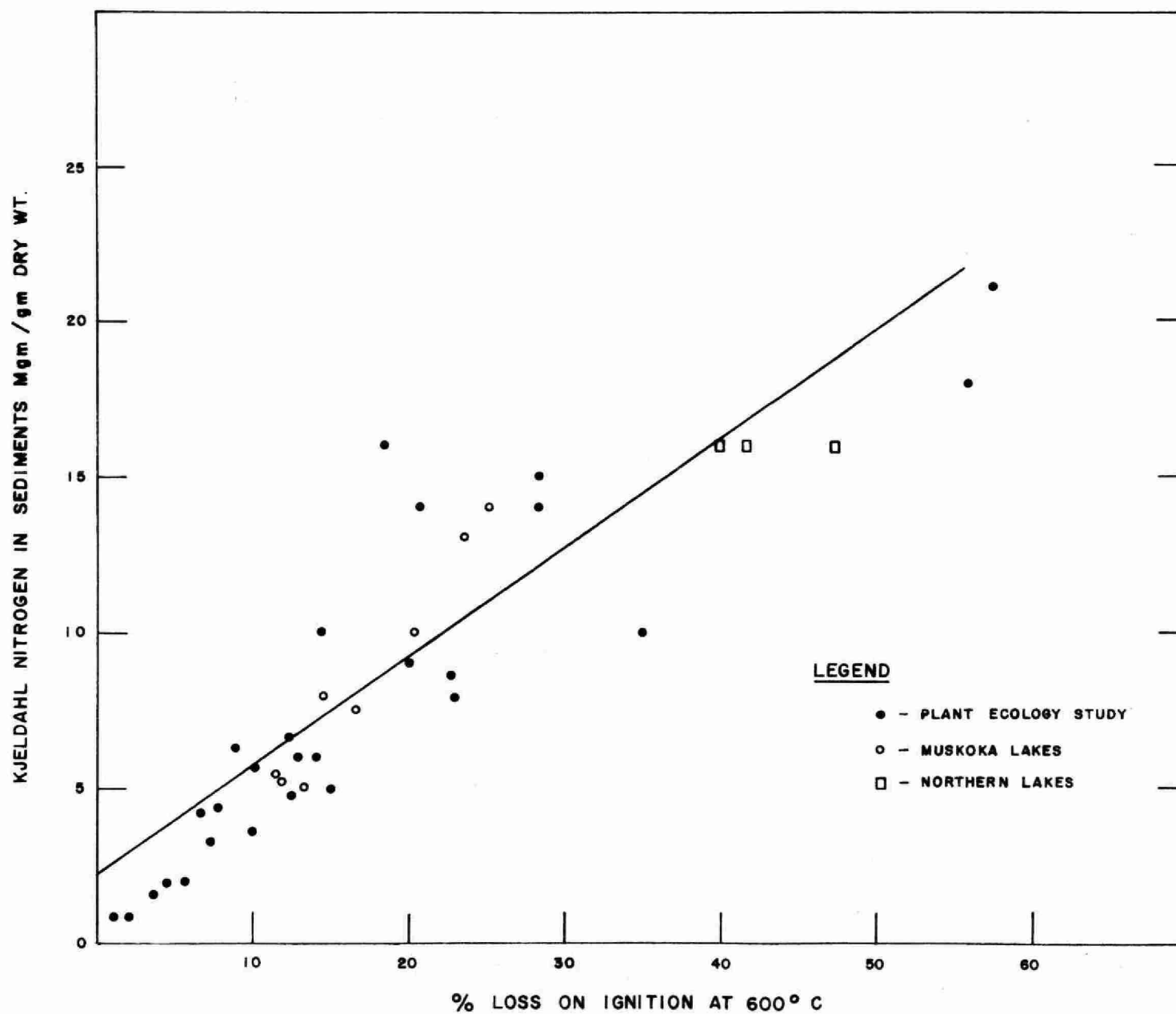
IMPOUNDMENT	TYPE	AGE	SURFACE AREA IN HECTARES	MAXIMUM DEPTH IN METERS	% LITTORAL	WATERSHED AREA IN HECTARES
01	Kettle Lake	Pleistocene	2	7	77	10
02	"	"	2	15	48	29
05	"	"	6	17	36	82
10	"	"	6	14	27	203
11	"	"	4	13	52	203
25	Mill Pond	1860-70's	2	2	75	1,390
15	"	"	3	4.5	45	643
16	"	"	0.5	3		180
17	"	"	17	4.5	44	14,700
04	Mill & Trout	"	6	5	44	1,500
21	Trout Pond	1890's	0.8	2	100	554
22	"	"	0.7	3	100	554
23	"	"	0.7	3.5	100	554
32	"	1930's	0.5	3.5		165
33	"	"	0.5	4.5		165
18	"	"	4	4	77	753
27	"	"	0.5	2.5	71	65
28	"	1950's	0.5	4	23	65
03	"	"	12	8	29	280
29	"	"	0.5	2		21
12	"	"	0.2	3	49	421
30	"	"	0.5	2.5		152
31	Recreational	"	1	2		62
06	Waterfowl	3 Years	0.5	1.5	100	208

The relation between total Kjeldahl nitrogen concentrations in the sediments and the percentage loss on ignition is shown in Figure I. The least square regression line has the equation:

$$\text{Kjeldahl nitrogen (mgms/gm dry wt)} = 2.3 + 0.345 (\% \text{ loss on ignition}) \dots 1$$

The loss on ignition is a measure of the amount of organic debris present (see Appendix I). The nitrogen measured by the Kjeldahl method is virtually all organic, since inorganic compounds are unlikely to interfere with the Kjeldahl test. Thus it would appear that the organic material present in all

FIG.-1
KJELDAHL NITROGEN IN SEDIMENTS
Vs
PERCENTAGE LOSS ON IGNITION AT 600° C



of the sediments contains a relatively constant fraction of organic nitrogen, and a relatively constant C:N ratio is indicated.

Finger and Wastler (1969) found that the percentage loss on ignition for sediment samples collected from a river and estuary was directly proportioned to the organic carbon content, which agrees with the results of this work. Substituting their equation:

$$(\% \text{ loss on ignition}) = 0.78 + 2.51 (\% \text{ organic carbon}) \dots\dots 2$$

into equation 1 gives a C:N ratio of 9.

Klein, 1962, reports an average C:N ratio for the solid fraction of domestic wastes as 9 within a range of 6 to 12. Finger and Wastler found similar values in sediments in areas known to be affected by domestic wastes, but much higher ratios (up to 42) in areas affected by industrial wastes. The ratio of 9 is lower than generally found in living plants and the cause of the relative concentration of nitrogen in the sediments is not readily apparent. Denton (1966) measured C:N ratios from 11 to 96 for a wide variety of aquatic plants. Since the carbon:nitrogen ratios for the unpolluted northern lakes are in agreement with the other lakes, domestic development and runoff from agricultural areas do not appear to have caused any significant changes in this particular character of the sediments.

For all 8 stations in Lake Muskoka, the lowest percentage loss on ignition values were recorded in late July and August. Other lakes analyzed in this study do not show seasonal variations as consistently but, in the majority of cases where sufficient samples were taken, the lowest values were observed in mid-summer. The exceptions were Lake 02 and one station in each of Lakes 05 and 03. It is quite possible that small variations in the position of the sampling site obscured the seasonal variations in these latter cases. All of the stations in Lake Muskoka were marked with buoys during the summer to assure a fixed sampling location.

The Kjeldahl nitrogen and total phosphorus concentrations in the sediments were not related in any way, nor was the phosphorus concentration related to the loss on ignition values. This suggests that phosphorus is present mainly in an inorganic form.

The correlation between total phosphorus and total iron concentrations in the sediments is shown in Figure 2. The line is a least squares fit and has the form:

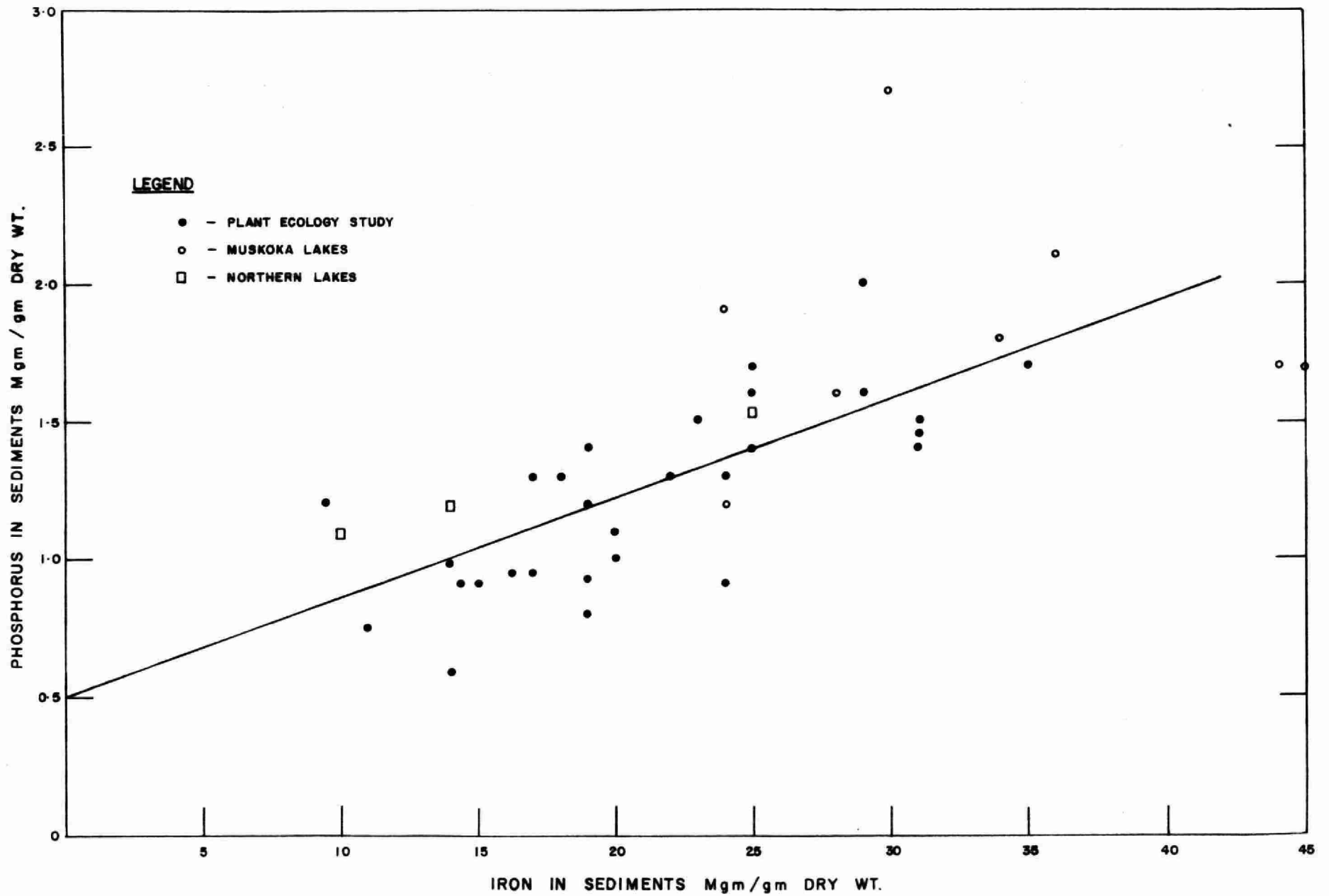
$$\text{Phosphorus (mgm/gm)} = 0.50 + 0.035 \text{ Fe (mgm/gm)} \dots 3$$

The correlation coefficient is 0.69. The trend exists even though some fraction of the iron content is probably in a physical form which cannot adsorb or react with phosphorus. The fundamental iron-phosphorus relationship is probably less variable than indicated by the data since there is no way at present to compensate for the presence of non-reactive forms of iron. The Fe:P weight ratio calculated from the slope of the line is 28.

Gorham & Swaine (1969), measured Fe:P ratios in oxidized crusts and sediments in Lake Windermere and Esthwaite Water and found values in the range of 54 to 70 for crusts and in the low twenties for deeper sediments. They attributed the lower ratios to the presence of organic matter containing phosphorus.

In this case, the greater the loss on ignition, the lower the Fe:P ratio will be, if the iron concentration is relatively constant. This conclusion does not apply to the present results. The correlation coefficient was - 0.5. While there was a tendency for the ratios above 20 to correspond to low loss on ignition, the ratios never approach the 50 - 70 range observed by Gorham and Swaine, even when the organic content approaches zero. The maximum ratio observed was 27. In cases of high organic content, the Fe:P ratios are not abnormally low, thus it appears that organic matter is not a major factor in establishing the Fe:P ratios.

FIG.-2
PHOSPHORUS Vs IRON IN THE SEDIMENTS



Seventeen field observations of iron and phosphorus concentrations, in the bottom waters, under anaerobic conditions, are plotted in Figure 3. (Wile, 1970). The weight ratio of iron to phosphorus from the slope of the least square (feet) is 7.6. Equivalent values from Lake Muskoka averaged 9:1 for 6 measurements, (*Michalski, 1970). The apparent simultaneous loss of iron and phosphorus from solution in Lake Erie observed by Bennett and Brydges, (1969) corresponded to a weight ratio of 8. It is therefore reasonable to postulate that the formation of iron-phosphorus sediments under oxidizing conditions and their decomposition and release under reducing conditions are major factors in controlling the phosphorus concentrations in both the sediments and the lake water.

Increasing iron concentrations in the sediments regularly corresponded to increased manganese concentrations, Figure 4. The line is a polynomial regression of degree 2 of the form:

$$\text{Mn (mgm/gm)} = 0.82 - 0.066 \text{ Fe} + 0.002 \text{ Fe}^2 \dots\dots\dots 4$$

There is a decrease in the Fe:Mn weight ratio as concentrations increase, Table 2.

TABLE 2

Iron manganese in sediments and the corresponding Fe:Mn ratios read from Figure 4.

Fe mgm/gm	Mn mgm/gm	Fe:Mn
20	0.45	44
30	1.0	30
45	2.7	17

Gorham and Swaine (1969), found an average Fe:Mn ratio of 6.6 in sediments with total iron concentrations of about 70 mgm/gm.

*Private communication.

FIG. - 3

IRON IN THE HYPOLIMNION Vs PHOSPHORUS IN THE HYPOLIMNION FOR LAKES IN THE PLANT ECOLOGY STUDY

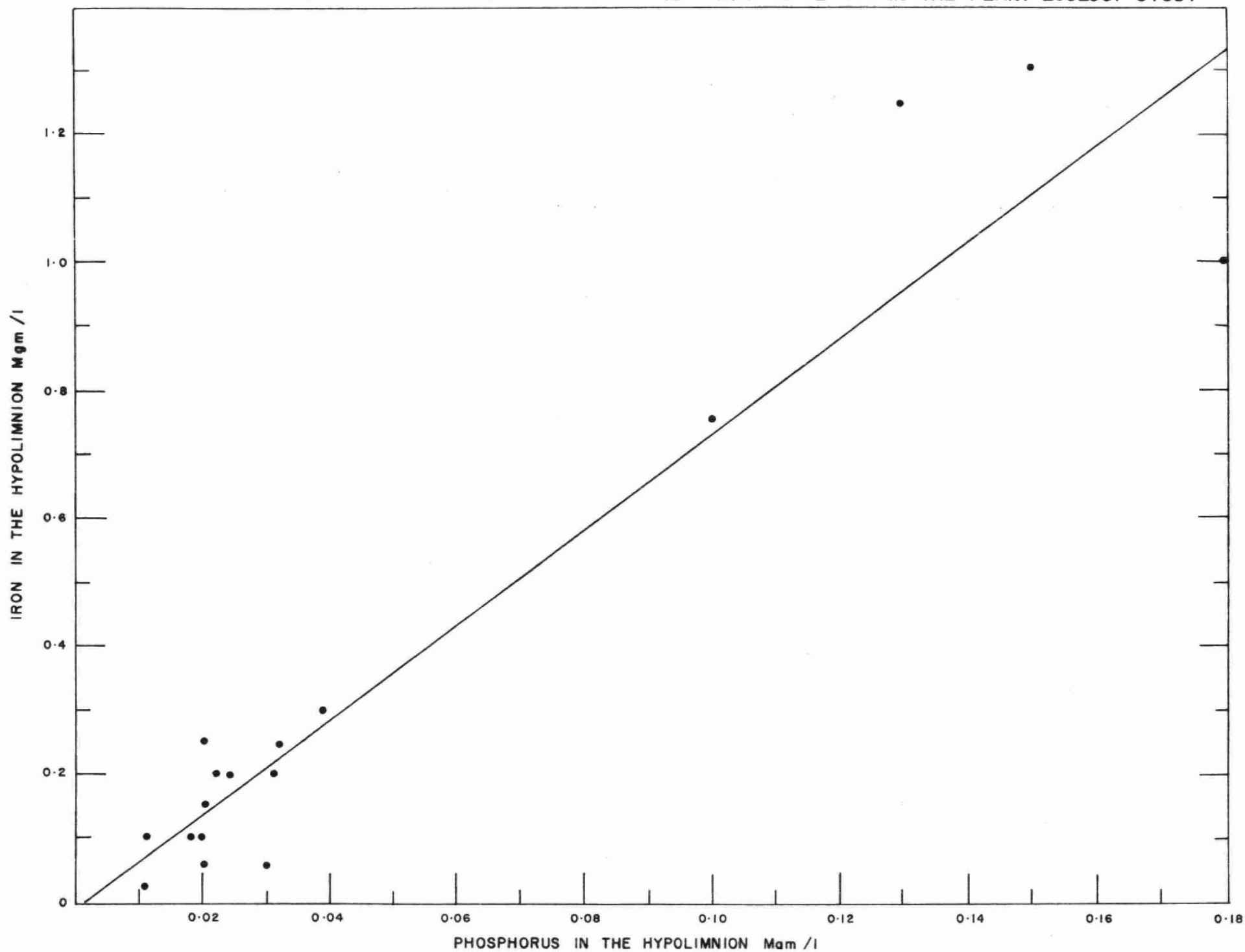
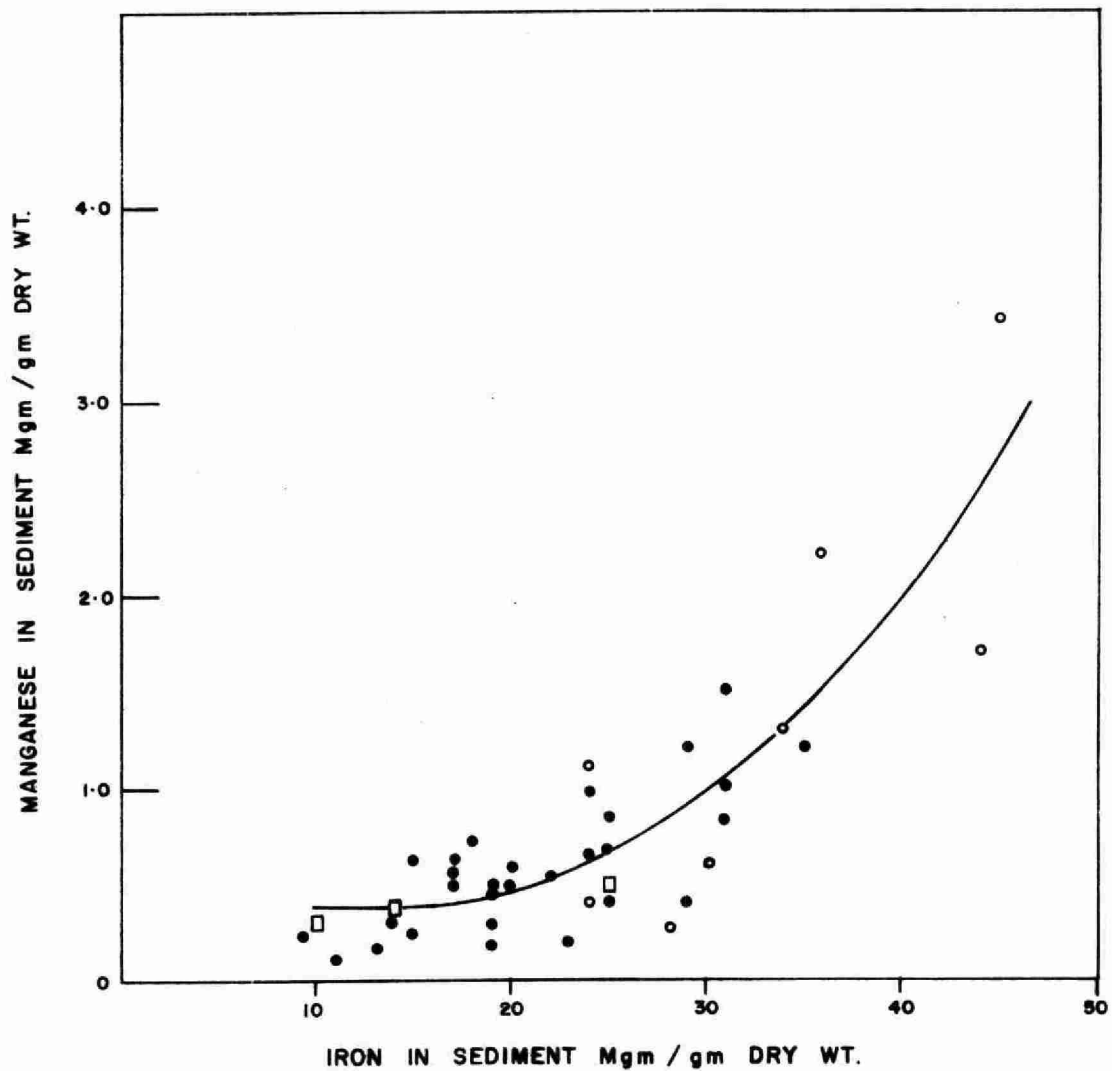


FIG.- 4
MANGANESE Vs IRON IN SEDIMENTS



LEGEND

- - PLANT ECOLOGY STUDY
- - MUSKOKA LAKES
- - NORTHERN LAKES

The concentrations of iron and manganese in Lake Muskoka sediments are greater in the deeper water than in the shallower bays, with manganese showing a more pronounced effect. The average iron and manganese concentration were 40 and 2.1 mgm/gm respectively in the open lakes and 27 and 0.51 mgm/gm respectively in the bays.

The weight of the dry residue from unit volume of wet sediment is measured as part of the triple A test. This weight is of course inversely proportional to the water content. The dry weight per cubic centimeter of wet sediment is plotted against the total Kjeldahl nitrogen concentration in Figure 5.

The line has the equation:

$$(\text{Kjeldahl nitrogen} + 0.2) \times (\text{dry wt./cc}) = 1.50 \dots\dots 5$$

The constant 1.50 was the average value of the nitrogen X dry weight product and the factor 0.2 was added to improve the fit for low nitrogen concentration. Since density of finely ground sand is approximately 1.2 - 1.4 gm per cc., values for the dry weight greater than this would be impossible. Such a sediment would be about 40 - 50% water by volume. The highest dry weight recorded was 1.09 gm/cc. As the Kjeldahl nitrogen concentration increases the dry weight decreases sharply until it corresponds to only about 5% of the total weight. At the same time the water content correspondingly increases. Since the Kjeldahl nitrogen and percent loss on ignition are related, Figure 1, the dry weight and loss on ignition are also related, as shown in Figure 6.

The line has the equation:

$$(\% \text{ loss on ignition} + 1) \times (\text{dry wt/cc}) = 3.23 \dots\dots 6$$

The constants were evaluated in the same manner as for equation 5.

FIG. 5

DRY WEIGHT OF SEDIMENT gm/cc

V_s

TOTAL KJELDAHL NITROGEN IN SEDIMENT Mgm / gm DRY WT.

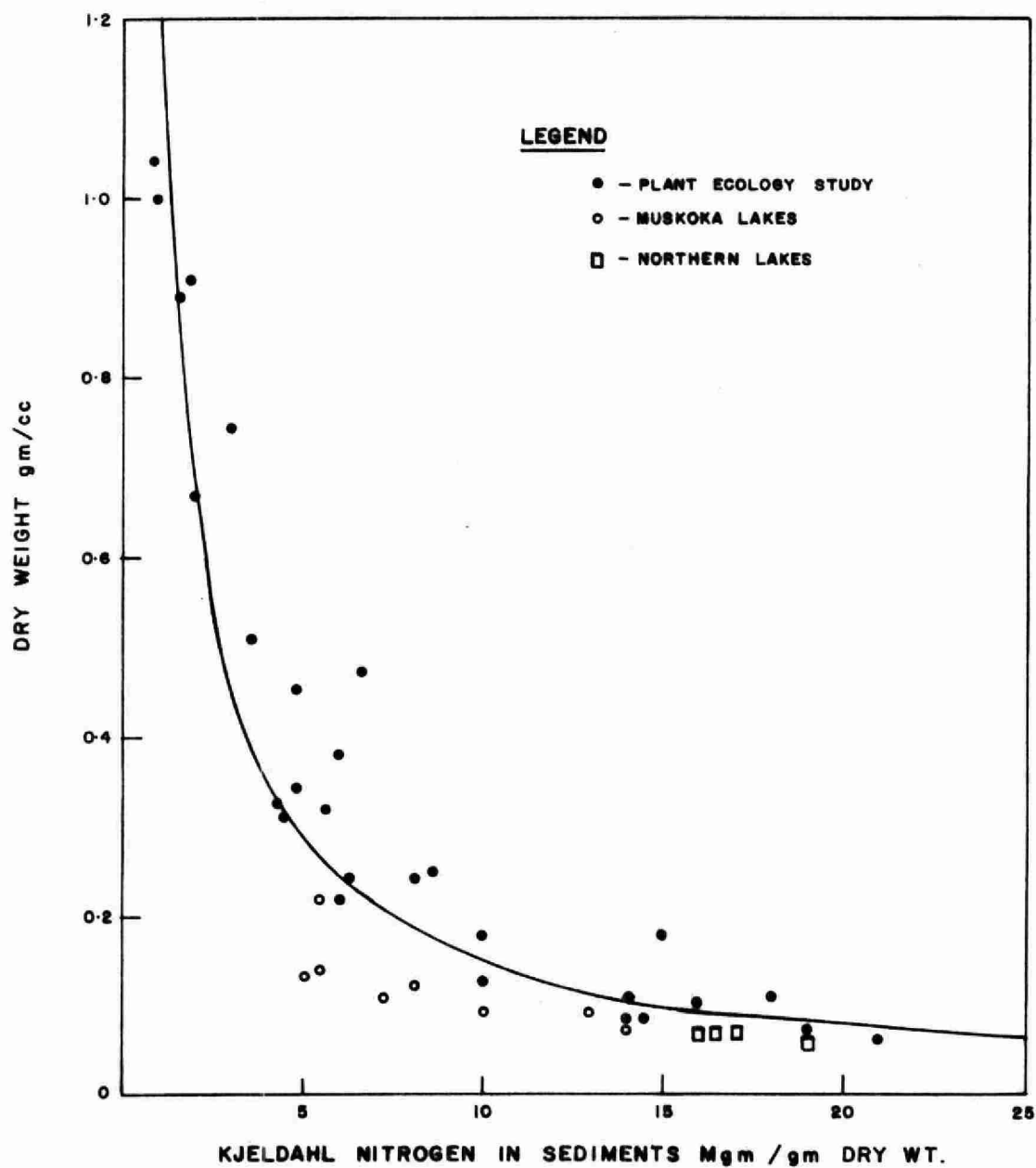
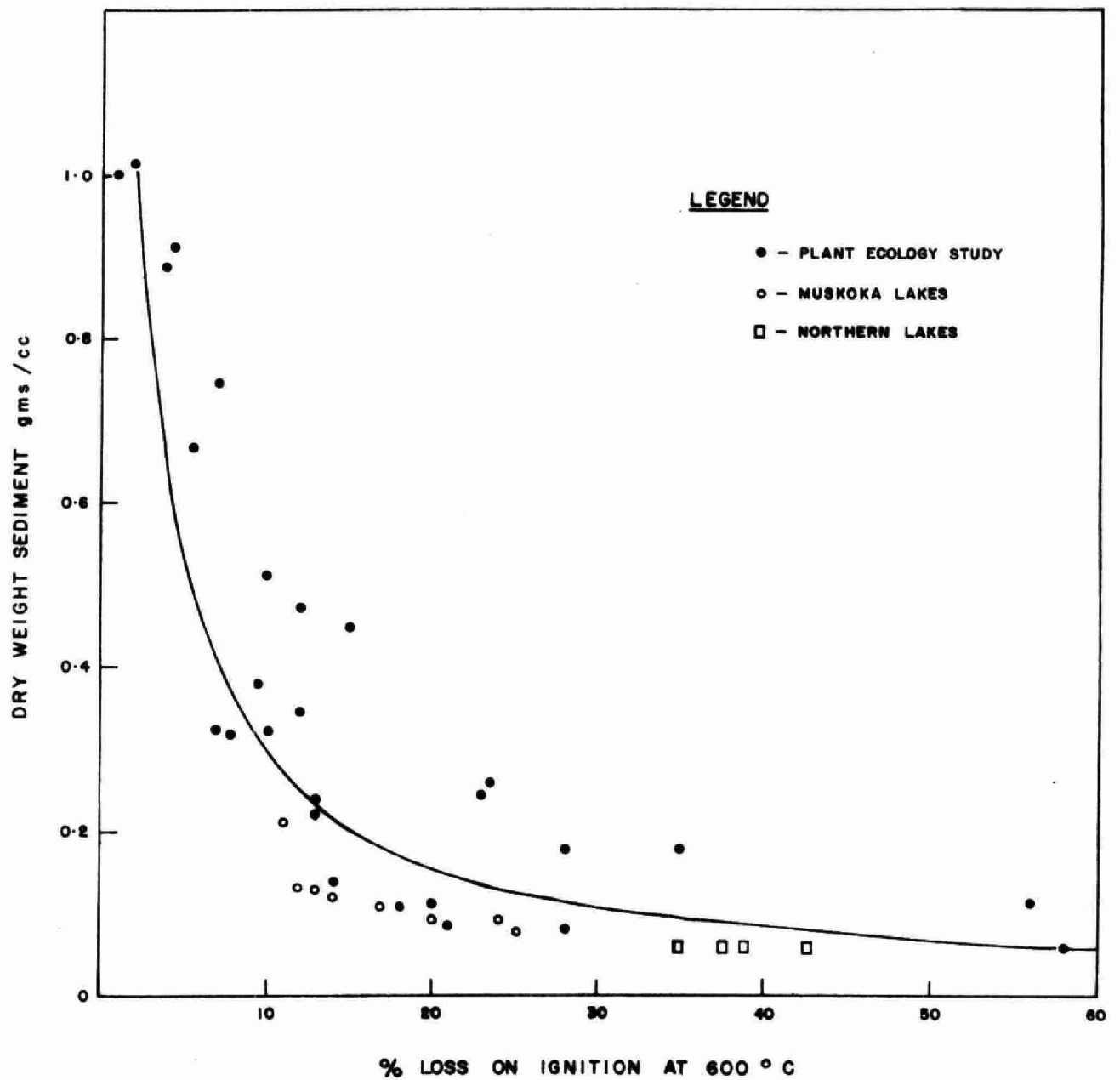


FIG. 6
DRY WEIGHT OF SEDIMENT PER CC
Vs
PERCENT LOSS ON IGNITION



The decrease in dry weight is not a result of mixing the more dense sand and less dense organic material. If it were, then there would be a nearly linear relationship between the weight and the amount of organic matter present and the ultimate dry weight would not go below about 0.5 gm/cc. Further evidence that factors affecting water content are more complex than are accounted for by simple mixing is obtained by drying sediment and then putting the water back. A 50 ml sample of sediment from station Muskoka - 5 which was completely stable with respect to further settling of solids, was dried overnight at 110°C. The dried material occupied about 10 - 15 cc. When the water level was made up to the original 50 ml and mixed, the final volume of wet sediment was only 16 cc., the rest being clear water. Similar results can be obtained for any sediment with the possible exception of the very pure sands. The experiment casts serious doubts about physical measurements made on previously dried sediments.

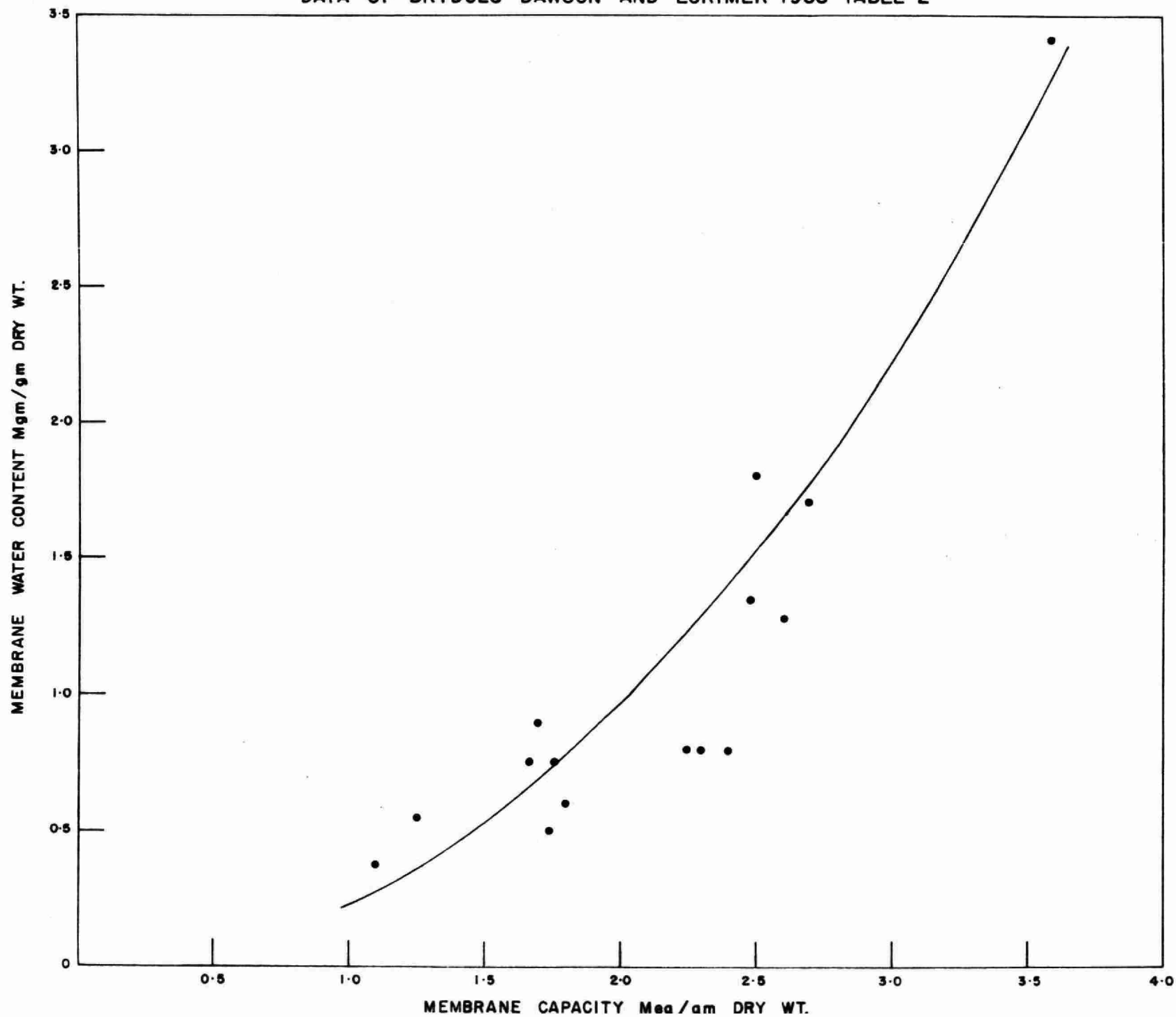
The Kjeldahl nitrogen value will include mainly protein type debris which is a well known ion-exchange material (Helfferich, 1962). Therefore, the sediments act as ion exchange resins, or more correctly gels, probably with the nitrogen corresponding to the fixed charge groups. It is also known that many proteins become less hydrophilic on denaturation (Ferry, 1948). A mechanism of this type may be partly the cause of the reduced water content of the sediments after heating. The effect of variable fixed charge concentrations on water content of ion exchange material can be seen in Figure 7, prepared from data of Brydges, Dawson and Lorimer, (1968, Table 2). The plot ignores any variations in cross linking which is the explanation of the variable water contents at given capacities. The line has the form:

$$(\text{Water content}) = 0.22 (\text{capacity meg/gm})^{2.1} \dots\dots 7$$

and was obtained from a log-log graph of the data.

FIG. 7

MEMBRANE WATER CONTENT Mgm/gm DRY WT. Vs. MEMBRANE CAPACITY Meg/gm DRY WT.
DATA OF BRYDGES DAWSON AND LORIMER 1968 TABLE 2



The rise in water content in this material corresponds well to the changes observed for the sediments. The water contents of the sediment are considerably greater than for the resin material. This is expected because the sediments are not made of a cross linked matrix but rather a loose material with the only compacting force being gravity. It seems justified to conclude that the Kjeldahl nitrogen in the sediments may control their water contents and possibly impart an ion-exchange resin character. The existence of inorganic ionic exchange capacity of the nitrogen is not defined by this work.

Measurement of ion exchange and adsorption capacity of sediments has been the objective of numerous studies. Both mechanisms imply that for any given sediment and ion there will be some equilibrium concentration between the liquid and solid phase. Experiments designed to measure these concentrations have lead to highly confusing results. In view of the obvious destruction of sediment properties by drying recorded here and also reported by Jackson, (1965) adsorption measurements made on dried material can barely be accepted as accurate.

Most attention has been focussed on the adsorption of phosphorus owing to its importance in the process of eutrophication. Pomeroy (1963), found adsorptive processes to be trivial in exchange between estuarine water and suspended matter. In 1965, for samples from a different area he found equilibrium concentrations of 25 - 50 parts per billion as P in solution in the laboratory. He did not report any observed field results. Hayes (1958), found equilibrium concentrations of 2.8 ppb and Hepher (1966) found 25 ppb but neither indicates whether these are total or soluble concentrations. If either of these mechanisms is operative, only soluble concentrations are to be considered.

Harter (1968), measured significant adsorptive capacity of sediments but his water concentrations were from 400 to 400,000 ppb as P and if the data is extrapolated to "natural" concentrations of the order of 10 ppb, then this mechanism seems to be unimportant. Such experiments are not easy to conduct because bacteria can also "adsorb" phosphorus and it is difficult to separate their effect from inorganic processes. Even if this can be achieved it is then a problem to relate the results to field conditions. Recently, Gumerman, 1970, has tried to separate the two effects by sterilizing Central Lake Erie sediment with tetracycline. He was able to demonstrate adsorption amounting to about one percent of the total sediment concentration. The measurements of equilibrium concentrations in contact with the sediment upon removal of phosphorus from solution, to simulate controlled inputs to Lake Erie, gave values slightly greater than 0.100 ppm as PO_4 , while the observed value for this area is less than 0.050 ppm (IJC report 1970). Therefore the laboratory result cannot possibly reflect real conditions, otherwise the phosphorus concentration in Central Lake Erie would tend to rise to double the present value. This area is known from phosphorus loading data to be depositing phosphorus in the sediment.

In one experiment carried out on dried Lake Erie sediment as part of the present study, an equilibrium concentration of 0.12 ppm P was observed which is far above the soluble phosphorus concentrations in the lake.

The apparent adsorption of phosphorus from solution by iron observed in Lake Erie, and the very similar Fe:P ratios observed in cases of release under anaerobic conditions strongly suggest that adsorption of phosphorus by iron is of great importance. In many areas the iron may become "saturated", and consequently any further adsorption measurements may show little effect. Of course, the opposite effect also can happen. Therefore, water chemistry as well as loadings of iron and phosphorus may have to be accurately examined as part of any discussion of adsorptive ability of the sediment.

Triple A Test.

The analytical results for all of the Triple A tests carried out are given in Appendix 3. All values are expressed as micrograms of material released from a gram of dry sediment (ppm) under the specified conditions of the test. Each extraction procedure was set up in duplicate and the reported analytical results are the average of the two.

While very little direct attention has been given to adsorption and equilibrium concentrations in this work, it was recognized very early that there was a minimum water:sediment ratio required in order to make the amount of material released dependent on the sample. If too much sediment was added to a given volume of water the concentrations of some parameters would not be proportioned to the amount of sediment. The ratios of greater than 175:1 used here were found to be well within a satisfactory range. The area of difficulties was not clearly defined as a general rule but was of the order of 50:1 by weight.

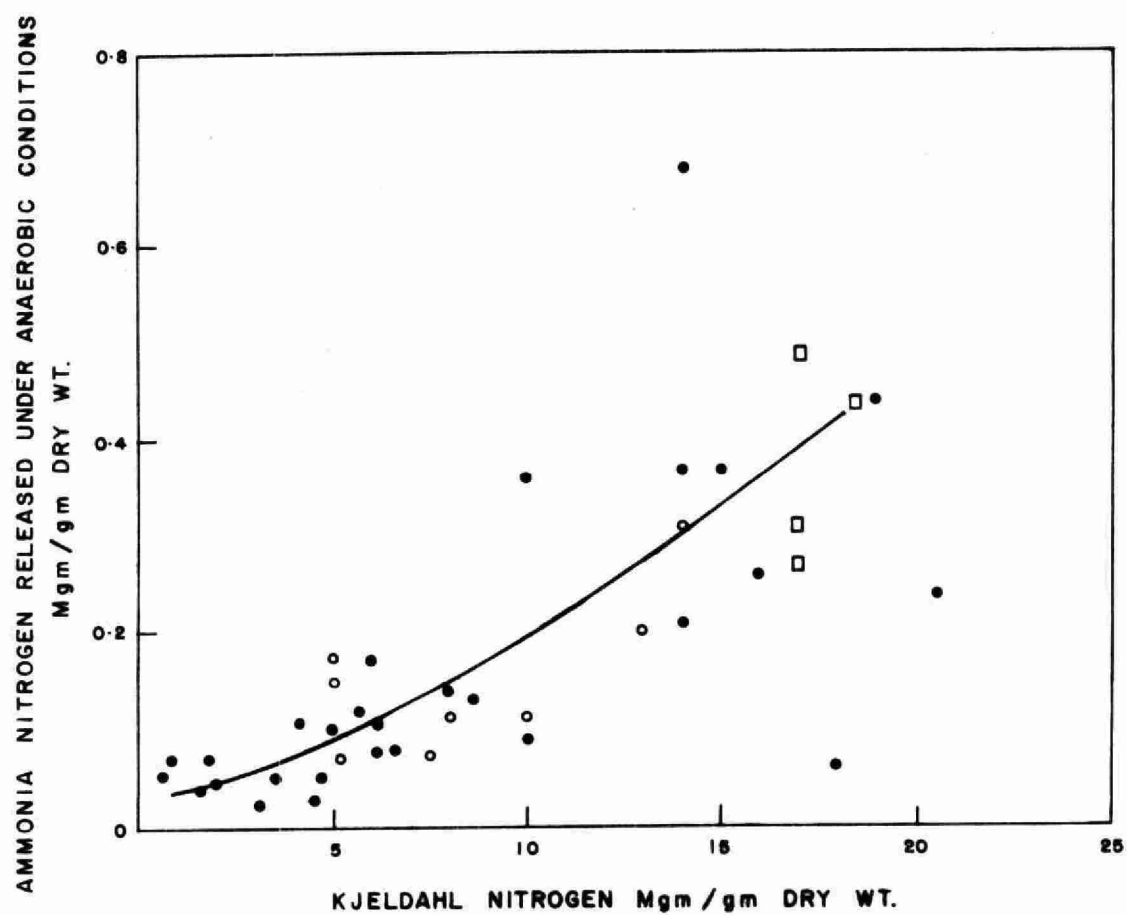
The ammonia nitrogen released was related to the total Kjeldahl nitrogen concentration in the sediment (Figures 8 and 9). The lines are the best fit polynomials to degree 2 and have the forms:

$$\begin{aligned} (\text{Ammonia released/gm-anaerobic}) &= 0.023 + 0.0116 (\text{nitrogen}) + \\ &\quad 0.00058 (\text{nitrogen})^2 \quad \dots 8 \quad \text{and} \\ (\text{Ammonia released/gm - aerobic}) &= 0.028 + 0.009 (\text{nitrogen}) + \\ &\quad 0.00089 (\text{nitrogen})^2 \quad \dots 9. \end{aligned}$$

In both cases the nitrogen in the sediments is expressed in mgms/gm dry weight. There was very little difference between aerobic and anaerobic conditions. The results strongly suggest that nitrogen is recycling as a result of breakdown of organic matter. The maximum amount of nitrogen released was about 3 percent of the total in the sediment.

FIG. 8

AMMONIA NITROGEN RELEASED FROM SEDIMENTS UNDER ANAEROBIC CONDITIONS IN
Mgm / gm DRY WT. Vs TOTAL KJELDAHL NITROGEN IN THE SEDIMENTS



LEGEND

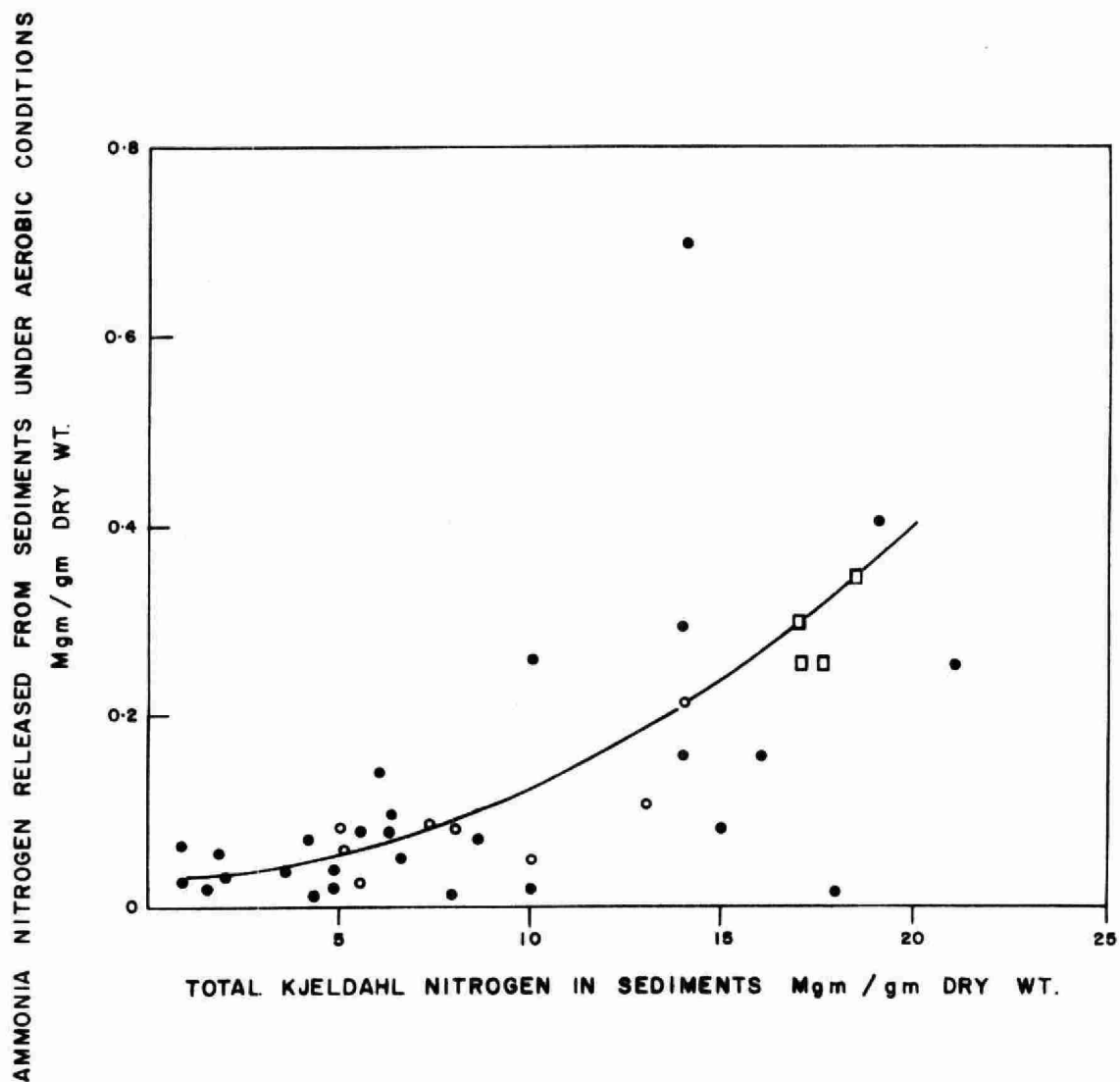
- - PLANT ECOLOGY STUDY
- - MUSKOKA LAKES
- - NORTHERN LAKES

FIG. 9

AMMONIA NITROGEN RELEASED FROM SEDIMENTS
UNDER AEROBIC CONDITIONS Mgm/gm DRY WT.

Vs

TOTAL KJELDAHL NITROGEN IN THE SEDIMENT
Mgm/gm DRY WT.



LEGEND

- - PLANT ECOLOGY STUDY
- - MUSKOKA LAKES
- - NORTHERN LAKES

One station in each of lakes 1 and 2 were exceptional in that the high concentrations of Kjeldahl nitrogen did not correspond to high ammonia concentration released. The reason for this is not known.

The amount of phosphorus released to the water under aerobic conditions was generally very small, and was not related to the total concentration in the sediments. For most samples, less than 5 percent and more often about 1 percent of the total was found to be released to the water. These results indicate that phosphorus recycling from aerobic sediment is rather low and is negligible in terms of possible concentrations which could be established in the overlying water. Kemp, 1970, found similar results when extracting phosphorus with weak boric acid solutions. He measured extractable phosphorus on over 120 Lake Ontario samples and found 35 ppm as the maximum amount released while most samples released less than 7 ppm.

However, Lakes 05, 10 and 11 appear to be exceptions to the general observation of negligible recycling of phosphorus under aerobic conditions. Three samples from lake 10 and 2 from lake 05 released amounts of phosphorus well above the overall average. The reason for the greater release of phosphorus from these sediments is not established to date.

In contrast to the aerobic results, substantial amounts of phosphorus are released under anaerobic conditions. This result is well known in nature and is observed in many lakes where the hypolimnion becomes devoid of oxygen. The soluble phosphorus released is proportioned to the total phosphorus in the sediment - Figure 10. The line is a fitted polynomial and has the equation:

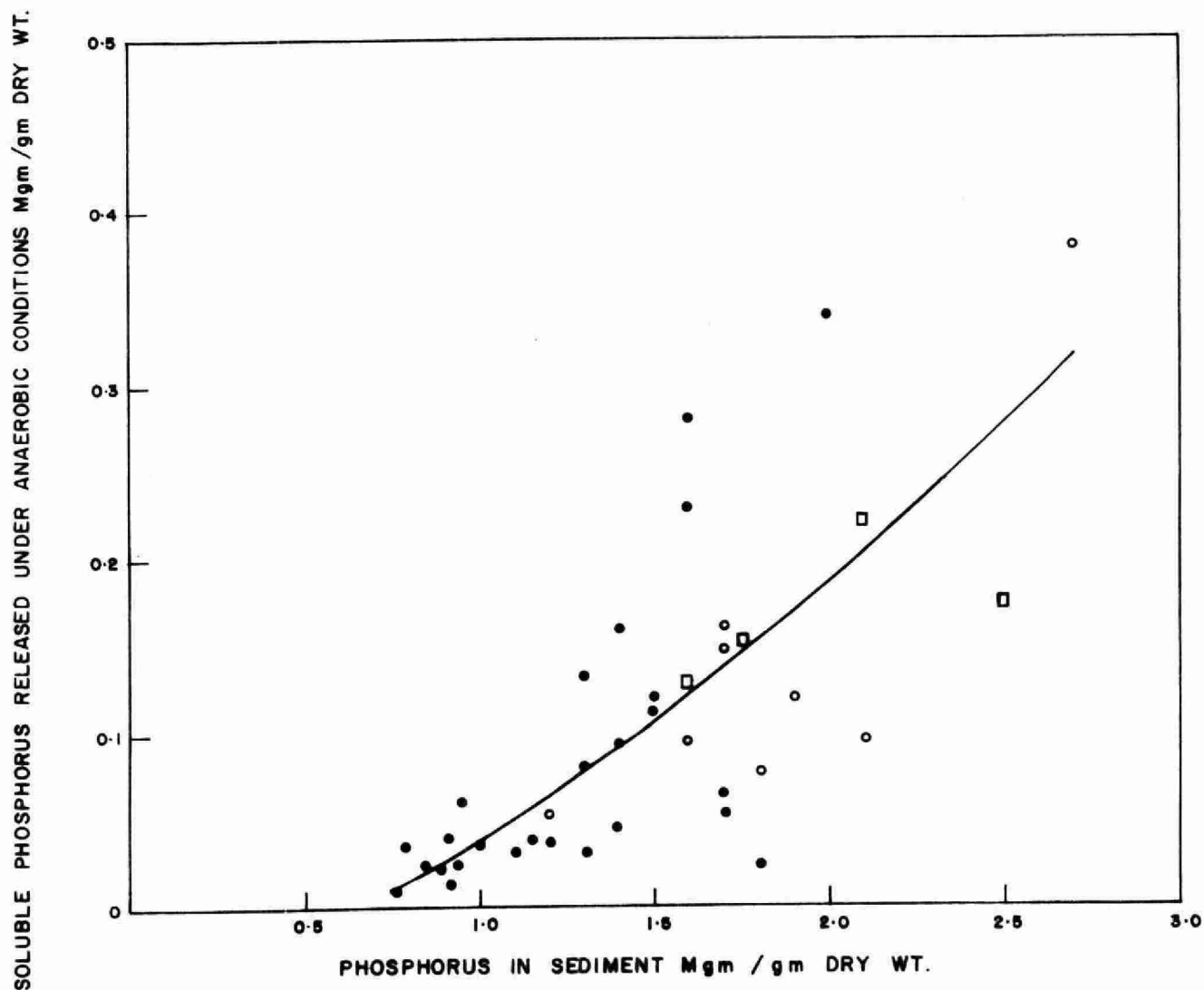
$$(P \text{ released}) = -0.062 + 0.080(P \text{ mgm/gm}) + 0.022 (P \text{ mgm/gm})^2 \dots 10$$

FIG. 10

SOLUBLE PHOSPHORUS RELEASED FROM SEDIMENTS UNDER
ANAEROBIC CONDITIONS IN Mgm/gm DRY WT.

Vs

TOTAL PHOSPHORUS IN THE SEDIMENTS IN Mgm/gm DRY WT.



LEGEND

- - PLANT ECOLOGY STUDY
- - MUSKOKA LAKES
- - NORTHER LAKES

At total phosphorus concentrations in the sediment of 1 mgm/gm, less than 10 percent of the phosphorus is released while at 2.5 mgms/gm about 20 percent is released. It is interesting to note that Lakes 05 and 10 release similar amounts of phosphorus under both aerobic and anaerobic conditions. Lake 05 samples released 0.23 and 0.32 mgms/gm dry sediment respectively and lake 10 samples released 0.1 and 0.23 mgm/gm of dry sediment respectively.

Phosphorus released to the water under anaerobic conditions can be an important source. For example, sediment at station Muskoka-1 can release 0.030 mgms per cm depth of wet sediment. This much phosphorus alone released to 30 feet of water could cause excessive algae growths^{*} (Christie, 1970).

The weight ratios of iron to phosphorus released from sediments from the plant ecology study in the Triple A anaerobic extraction tests ranged from 1.5 to 19 and averaged 5.8. All of the sediments released small quantities of both iron and phosphorus, consequently analytical variations caused wide variation in the Fe:P ratios. Lake Muskoka sediments generally released more of both iron and phosphorus and the Fe:P ratios ranged from 4 to 6.5 for bay samples and 12 to 15 for open lake samples.

The iron:phosphorus ratio observed in the field at Muskoka-1 under anaerobic conditions averaged 9 and ranged from 5 to 19 over 6 measurements. The anaerobic Fe:P ratios for laboratory and field results are relatively close which supports the use of the Triple A test as an estimate of potential field effects. Presumably, the same basic effect is taking place in both cases. There are not sufficient data collected to compare the absolute amounts released in the laboratory and actual values measured in the field.

* Private communication.

The fact that only a fraction of the total phosphorus is released leads to consideration of what other forms are present. Organic phosphates certainly must account for at least part of the total. Iron compounds resistant to solution either naturally or through protection by surface coatings of other material would continue to hold phosphorus under anaerobic condition.

A sample of Lake Erie sediment was recycled between aerobic and anaerobic conditions with removal of the solution each time. After 6 complete cycles, over 90% of the total phosphorus had been released to the water. During this time the sediment sample was broken up more and more until the experiment was discontinued because the fine particles were going through the glass fibre filters. The experiment supported the theory that all of the phosphorus is held in combination with iron compounds and the fact that only a fraction is released on one exposure to anaerobic conditions is due to the particular character of the sediment at the time of sampling. Because of the serious deterioration of the sediment, the experiment is of little relevance to field conditions - where sediments are known not to be similarly "destroyed". Pomeroy, et al. (1965) also observed that, when sediment was washed repeatedly to determine its ultimate ion-exchange capacity, the material broke up until it could not be removed by centrifugation.

The Triple A test is carried out so that the amount of material released is independent of the volume of water employed. Therefore, the results must indicate a potentially available fraction of any element under a single change of conditions, for example, from aerobic to anaerobic.

S U M M A R Y

The Kjeldahl nitrogen concentration in the sediments was proportional to the percentage loss of weight on ignition, confirming that the nitrogen is in an organic form. The carbon:nitrogen ratio was relatively constant for lakes with a wide range of productivity.

The water content of the sediments increased rapidly with increasing nitrogen and organic material content and reached about 90% by weight for 15 mgms of nitrogen per gram of dry material and 30% loss of weight on ignition.

The organic nitrogen, which is likely to be mostly proteins, apparently forms a stable gel.

The ability of the sediment to form stable gels of high water content in contact with water is essentially destroyed by drying. Ammonia nitrogen was released from sediments to distilled water in similar amounts under both aerobic and anaerobic conditions. The maximum amount released in seven days was about 3% of the total Kjeldahl nitrogen in the sediment. Total Kjeldahl nitrogen and total phosphorus concentrations in the sediments were not related.

The total phosphorus and total iron concentrations in the sediment were proportional indicating that an inorganic mechanism is most important in holding phosphorus in the sediments. The weight ratio of total iron to total phosphorus in the sediments averaged 19:1.

Phosphorus in the sediments was nearly insoluble under aerobic conditions, with generally less than 1% of the total being released to distilled water in 7 days at 5°C. Two lakes were discovered which were exceptions to this and contained sediments which released up to 17% of the total phosphorus under aerobic conditions. The controlling mechanism was not defined.

Many of the samples, particularly those from Lake Muskoka, released significant amounts of phosphorus under anaerobic conditions. Up to 25% of the total was released. The controlling mechanism is believed to be dissolution of iron compounds. The weight ratio of iron to phosphorus released under anaerobic conditions in the lab ranged from 4:1 to 15:1 compared to field observations of 9:1 for release from sediments under anaerobic conditions and 8:1 for apparent adsorption from solution.

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APPENDICES

Appendix I

Comparison of Conventional Loss on Ignition and Low Temperature Oxidation Methods.

The organic material content is an important characteristic of sediments. It has been routinely estimated by determining the loss of weight by a sample when heated to 600°C. The procedure certainly removes the carbonaceous material by oxidation. However, any other components, such as water of hydration, etc., which are volatile below the rather high temperature used will also be lost and thus recorded as "organic" material.

An instrument is now being marketed by International Scientific of Canada which exposes the sample to a flow of ionized oxygen gas. The ionization is accomplished at room temperature by application of the appropriate frequency radiation. The extremely reactive ionized oxygen then combines with the organic material and the resulting carbon dioxide is removed and can be recovered from the gas stream if desired. The only heat applied to the sample is from the heat of reaction which caused a temperature rise to approximately 150°C for the sediments analyzed.

The instrument company analyzed 10 samples measuring loss of weight only. The oxidized residues were returned and a routine loss on ignition test was carried out on six of them. Routine tests were also performed on the raw sample.

The results are presented in Tables I-1, I-2 and Figure I - 1.

Table I - 1

Comparison of Weight Loss from Sediments by Conventional and Low Temperature Oxidation.

Location	Conventional Method Wt. Loss %	Low Temperature Wt. Loss %
Lake Erie	6.1	2.4
Bay of Quinte	10.8	8.9
"	13.4	6.2
"	16.5	8.3

Table I - 2

Comparison of Weight Loss from Sediments by Conventional and low Temperature Oxidation.

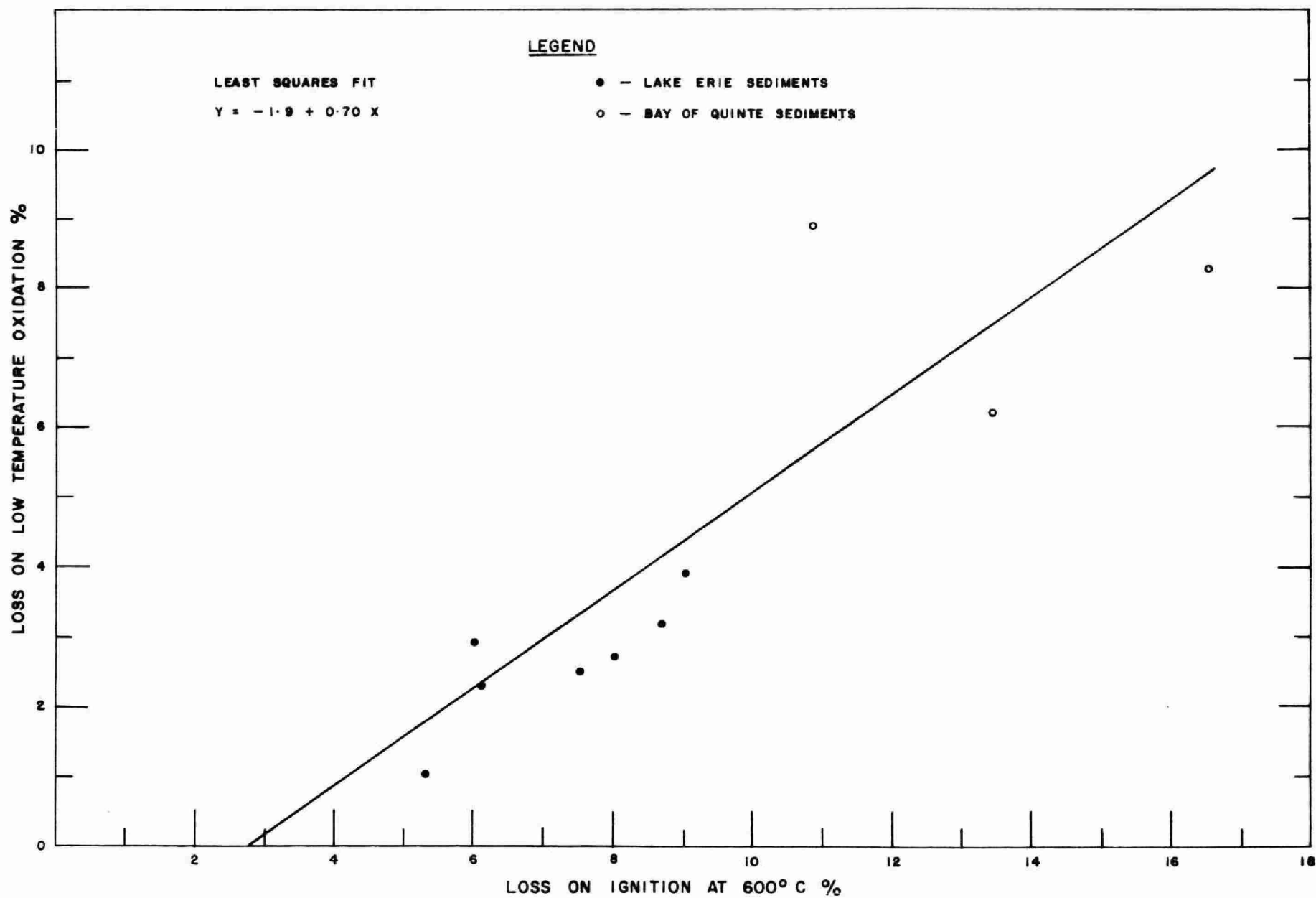
Location	Low Temperature Loss %	Conventional Wt. Loss from the Residue %	Total	Conventional Wt. Loss for Raw Sample %
Eastern Lake Erie	2.4	3.7	6.1	6.0
" " "	1.0	2.0	3.0	5.3
Western Lake Erie	3.2	5.2	8.4	8.7
" " "	2.5	4.5	7.0	7.5
" " "	2.7	4.0	6.7	8.0
" " "	3.9	5.0	8.9	9.0

The loss of weight at the low temperature is considerably less than by the conventional method. The close agreement between the combined low temperature and routine method and the routine method on the raw sample indicate that the same material is being removed by both methods.

The low temperature unit offers the possibility of recovering the CO_2 from the gas stream and thus obtaining the actual amount of carbon or of any of the other volatile materials for which appropriate recovery methods are available.

The causes and importances of the discrepancies between the two methods can only be reliably discovered by further experiments.

FIG. A-1
LOSS OF WEIGHT ON LOW TEMPERATURE OXIDATION (SEE TEXT)
NO LOSS ON IGNITION AT 600° C IN PERCENT



APPENDIX 2

Sediment Analytical Data

Nitrogen, phosphorus, iron and manganese are expressed in mgm/gm dry weight of sediment.

Loss on ignition is in percent.

Dry weight is the weight in mgm of the residue recovered from 1 cc of wet sediment after drying at 110°C.

The results are identified by lake and station number and the values given are the station averages with the number of determinations given in the last column.

Station	N	P	Fe	Mn	LO I	Dry Weight	No.
01							
#1	19	1.5	23	0.18	28.0	70	3
#2	21	0.91	15	0.25	57.7	60	3
#3	22	1.7	25	0.30	39.6	66	1
02							
#1	6.0	1.3	24	0.97	12.8	219	3
#2	18	0.92	15	0.62	55.7	113	3
03							
#1	2.0	1.0	20	0.55	5.5	664	3
#4	15	1.7	35	1.2	28.2	179	3
#5	1.8	0.55	19	0.38	6.4	572	1
05							
#1	10	1.6	29	1.2	14.2	129	4
#2	14	0.95	17	0.49	28.3	82	3
#3	11	1.3	28	0.30	13.2	119	1
06	0.97	0.59	14	0.35	1.0	1000	2

Station	N	P	Fe	Mn	LO I	Dry Weight	No.
10							
#1	14	1.6	25	0.67	19.8	107	3
#2	16	1.2	9.5	0.26	18.4	102	3
#3	14	2.0	29	0.40	20.7	87	3
12	6.3	1.5	31	1.5	9.5	380	2
15							
#1	4.8	1.3	17	0.55	15.0	452	3
#3	3.3	0.94	19	0.28	7.2	747	2
#4	4.3	1.4	31	0.81	6.7	328	3
16							
#1	5.7	1.4	31	0.97	10.1	324	3
#5	4.1	1.1	21	0.19	6.2	532	1
17							
#1	0.95	0.78	19	0.49	1.8	1041	4
#2	1.9	0.88	24	0.65	4.3	913	3
18							
#1	7.8	0.98	14	0.28	21.3	240	1
#2	10	1.2	19	0.50	35.1	180	4
#3	8.3	1.3	15	0.49	17.7	228	1
27	6.6	1.4	25	0.83	12.3	473	4
29	4.4	1.3	22	0.53	7.8	319	4
30	6.3	1.1	20	0.59	13.9	242	4
31	3.6	0.94	17	0.58	10.2	514	4
32	8.1	1.3	18	0.71	22.9	246	4

Station	N	P	Fe	Mn	LO I	Dry Weight	No.
Muskoka							
#1	14	2.7	30	0.57	25.2	78	27
#2	5.0	1.7	44	1.7	13.3	132	5
#3	5.2	1.7	45	3.4	12.0	134	5
#4	10	1.6	28	0.27	20.3	92	7
Rosseau							
#5	8.1	1.8	34	1.3	14.4	124	5
#6	5.5	1.2	24	0.41	11.4	218	8
Joseph							
#7	7.2	2.1	36	2.2	16.8	111	5
#8	13	1.9	24	1.1	23.6	95	24
Northern Lakes							
B	16	1.6	25	0.50	40.3	-	10
C	16	1.1	10	0.32	47.5	-	10
D	17	1.2	14	0.39	41.6	-	10

APPENDIX 3

Triple A Test Analytical Data

Results are expressed as micrograms released from 1 gram of sediment on a dry weight basis. The results are identified by lake and station number and the values given are the station averages with the number of determinations given in the last column.

NO₃ - nitrate as N
 NH₃ - ammonia as N
 N - total Kjeldahl nitrogen as N
 TP - total phosphorus as P
 SP - soluble phosphorus as P
 Fe - iron
 Mn - manganese
 Ca - calcium

Part I - Aerobic Conditions

Sample	NO ₃	NH ₃	N	TP	SP	Fe	Mn	Ca	No.
01									
#1	12	407	1400	66	50	100	0	1,500	3
#2	20	260	870	40	20	290	0	2,600	2
02									
#1	9	140	220	57	100	140	5	7,100	3
#2	5	13	80	20	5	70	0	11,000	3
03									
#1	8	30	65	14	11	135	3	2,400	2
#4	4	85	680	130	15	240	5	12,000	2
#5	4	10	30	7	2	30	0	-	1
05									
#1	11	260	1040	90	68	170	7	1,800	3
#2	4	160	510	46	30	110	0	8,300	3
#3	7	20	320	31	10	120	0	7,000	1

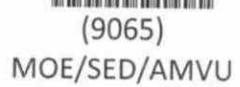
Sample	NO ₃	NH ₃	N	TP	SP	Fe	Mn	Ca	No.
06	5	25	50	17	25	430	4	1,350	2
10									
#1	17	300	350	105	160	285	2	9,700	3
#2	17	170	580	-	35	65	5	14,000	3
#3	20	700	1030	190	230	220	7	13,500	3
12	4	85	110	-	23	180	15	5,900	2
15									
#1	4	16	105	34	20	90	4	3,650	2
#3	2	2	25	9	4	60	2	3,000	2
#4	3	70	175	37	30	230	5	4,450	2
16									
#1	6	80	155	33	26	180	4	440	3
#5	5	70	-	-	20	200	1	-	1
17									
#1	7	62	75	27	12	460	4	2,100	4
#2	2	53	97	44	14	310	5	1,700	3
18									
#1	3	6	170	17	2	0	9	6,100	1
#2	7	14	205	16	4	13	7	6,300	3
#3	1	2	130	12	1	10	0	2,500	1
27	17	45	140	11	11	70	1	3,650	2
29	2	9	54	13	7	140	4	4,570	3
30	30	80	-	13	6	200	10	4,730	3
31	3	37	85	14	7	120	4	2,100	3
32	10	11	290	40	11	100	0	5,770	3

Sample	NO ₃	NH ₃	N	TP	SP	Fe	Mn	Ca	No.
Muskoka									
#1	22	210	480	54	23	680	200	2,860	23
#2	8	86	345	35	12	300	33	1,000	5
#3	9	76	185	23	11	305	188	1,000	5
#4	35	50	200	36	19	108	7	1,500	6
Rosseau									
#5	14	82	292	55	24	308	5	1,500	5
#6	18	27	100	14	9	100	17	750	6
Joseph									
#7	21	86	294	64	24	370	5	1,550	5
#8	26	110	340	61	25	136	79	1,400	19
Northern Lake									
A	90	260	-	-	34	0	0	2,600	1
B	23	260	-	23	18	780	50	2,600	1
C	37	300	-	25	20	50	20	2,500	1
D	3	350	350	44	41	60	30	2,900	1

Part II - Anaerobic Conditions

Sample	NO ₃	NH ₃	N	TP	SP	Fe	Mn	Ca	No.
01									
#1	17	440	-	130	120	170	0	1,570	3
#2	37	240	810	38	15	290	10	6,000	2
02									
#1	8	170	170	145	133	430	57	6,400	3
#2	6	63	190	44	40	140	35	10,000	3
03									
#1	3	50	100	40	35	180	20	2,000	2
#4	3	370	600	120	55	790	50	7,500	2
#5	1	20	80	19	12	80	3	-	1
05									
#1	9	360	1075	280	230	220	120	7,700	3
#2	4	203	550	70	64	70	7	8,300	3
#3	12	140	1000	60	50	250	0	6,000	1
06	10	65	60	-	56	645	9	1,650	2
10									
#1	8	370	450	180	280	235	35	8,400	3
#2	12	260	450	44	40	130	7	12,000	3
#3	13	680	960	270	340	240	7	11,500	3
12	2	80	180	-	115	280	75	4,400	2
15									
#1	3	50	185	70	80	130	25	3,150	2
#3	6	20	75	33	25	130	10	2,000	2
#4	3	110	260	95	95	145	20	4,000	2
16									
#1	3	120	300	150	160	220	37	3,500	3
#5	5	90	-	-	50	320	40	-	1

Sample	NO ₃	NH ₃	N	TP	SP	Fe	Mn	Ca	No.
17									
#1	7	65	65	43	37	430	10	2,200	4
#2	7	73	110	32	25	480	15	1,800	3
18									
#1	-	50	310	17	6	10	20	4,300	1
#2	12	90	540	50	37	63	53	3,900	3
#3	-	30	160	42	6	35	6	1,800	1
27	1	80	235	-	45	180	25	2,700	2
29	3	30	70	35	24	120	30	3,000	3
30	3	140	430	60	30	120	20	3,800	3
31	4	50	140	30	21	170	38	900	3
32	3	140	430	60	30	120	30	3,800	3
Muskoka									
#1	14	310	1060	420	380	1800	50	1,700	23
#2	9	175	545	264	148	2260	205	1,000	5
#3	6	150	450	220	158	2075	260	1,000	5
#4	6	104	365	130	93	360	23	1,500	6
Rosseau									
#5	8	110	310	120	76	1270	58	1,150	5
#6	4	70	208	66	56	360	10	600	6
Joseph									
#7	18	128	438	158	97	1120	145	1,250	5
#8	18	200	580	165	118	510	94	1,400	19
Northern Lake									
A	3	490	-	-	129	540	0	2,600	1
B	3	310	-	166	174	1,890	50	2,600	1
C	3	270	270	160	150	890	20	2,500	1
D	3	440	520	230	220	1,400	150	2,900	1



MOE/SED/AMVU
Brydges, T
Sediment analysis

amvu

c.1 a aa